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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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INVENTOR(S)

Given Name (first and middle [if any])	Family Name or Surname	Residence (City and either State or Foreign Country)
LINGJIE JAY	GUO	ANN ARBOR, MI

Additional inventors are being named on the ________ *separately numbered sheets attached hereto*

TITLE OF THE INVENTION (500 characters max)

A Spin-On UV-curable resist for Micro- and Nanolithography

Direct all correspondence to: **CORRESPONDENCE ADDRESS**

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ENCLOSED APPLICATION PARTS *(check all that apply)*

☒ Specification *Number of Pages* 8

☒ Drawing(s) *Number of Sheets* 1

☒ Application Data Sheet. See 37 CFR 1.76

☐ CD(s), Number

☐ Other (specify)

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Respectfully submitted,

SIGNATURE [signature]

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Date May 29, 2004

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[Page 2 of 2]

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A Spin-On UV-Curable Resist for Micro- and Nanolithography

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FIELD OF INVENTION

This invention relates the fabrication of nano- and micro- structures, as well as their potential applications. More specifically it represents a new material system that can be used for patterning various size features ranging from nm to mm using conventional contact exposure tools or other simple equipments.

DESCRIPTION OF THE PRIOR ART

Nano-patterning is an essential part of the nanotechnology research in order to fabricate nanostructures to harness their unique properties. However, in order for nano-devices and nanostructure fabrication to have significant practical value, a low-cost and high-throughput nano-patterning technique is indispensable. Among many new emerging lithography techniques that are aimed at addressing this issue, nanoimprinting technique is regarded as one of the most promising one. Nanoimprint has the capability of patterning sub-10 nm structures, yet only entail simple equipment setup and easy processing. It has been applied in the fabrication of numerous electric and optical devices. Wafer-scale processing has also been demonstrated. However, there are obstacles preventing the nanoimprint to be an omnipotent solution for the lithography needed for the next generation nano-scale devices, e.g. the high temperature and high pressure required during the imprinting, which is especially unsuitable for the microelectronics fabrication. Step-and-Flash Imprint Lithography (S-FIL) is another technique based on mechanical imprinting but uses UV curable liquid material as resist. The liquid resist are dispensed in droplet form onto the substrate, and then the template is brought into contact with the substrate and pressed against the substrate to spread out the liquid resist. Next the liquid resist is cured by UV light exposure. This process can be carried out at room temperature. However the thickness and the uniformity of the resist and the residual layer are difficult to control in this process because the resist film is formed by spreading under pressure. In addition, the UV curing formulations used in S-FIL are based on free radical polymerization of acrylic functional monomers and oligomers; such material system typically exhibits a much

higher shrinkage after cure and suffers from oxygen sensitivity issue: oxygen scavenges free radical species and inhibit polymerization process at the resist surface, making the process prone to defect generation. In order to achieve low viscosity for low pressure imprinting, reactive monomers are usually needed. Those monomers are volatile and give out very unpleasant odor.

SUMMARY OF THE PRESENT INVENTION

It is therefore the object of this invention to provide a new material system for nano- and microlithography using simple contact exposure tools or other appropriate equipments. By using an appropriate material as a thin undercoating, this liquid resist can be spin-coated onto a variety of substrates with high uniformity and the thickness can be precisely controlled. The low viscosity of this liquid system allows imprinting with low pressure and low temperature (e.g. room temperature). Adding organosilicone components to the resist formulation will not only increase the resist's dry etching resistance but also make it easier to be separated from the mask. This material system is also suitable for the Combined-Nanoimprint-and-Photolithography technique that we have developed (pending PCT application), which can greatly simplify the process of patterning nanostructures.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1. Representative structure of UV curable silicone epoxy materials. (I) di-epoxy oligomer; (II) cross-linker

Figures 2-6 shows various sizes of patterns that have been achieved with the new uv-curable material system. Patterns as large as tens of microns and as small as 20 nanometers can be easily obtained. Figure 6b shows a Au/Ti nanodot arrays produced by a lift-off process.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The material system we developed for nano- and microlithography are based on cationic crosslinking of cycloaliphatic epoxies. Because cationic polymerization is not oxygen inhibited, it should generate fewer defects if used as UV curable imprinting resist. In addition, low photoinitiator concentrations can be used. Moreover, the shrinkage of the cycloaliphatic epoxies

after curing is known to be low compared with acrylic systems. This low shrinkage provides several advantages as imprinting resists. The mold pattern can be accurately and faithfully replicated. Shrinking after curing tends to cause the film to delaminate from the substrate, especially on some difficult substrates such as metal and plastics. Therefore low shrinkage can ensure better film adhesion on those substrates.

We have developed novel material systems based on cationic polymerization of epoxy functional group as a nanoimprint resist. The liquid resist contains a silicone-diepoxy monomer (representative example **I**, Fig. 1), a silicone cross-linking agent (representative example **II**), and a photoacid generator. In addition, solvent can be added to achieve low viscosity for thin films. A thin under-coating layer is used for the better wetting of substrate by the liquid resist during spin-coating. This under-coating can also be used as the sacrificial layer in a lift-off process. Due to low viscosity and oxygen insensitivity, such material can be patterned using very simple experiment setup, and the presence of silicone provides a good mold release after the patterning. Micron scale and nano-scale patterns have been demonstrated with this material system using a conventional contact aligner, and UV curing is done with 365 nm light.

Material components

The material system comprises ingredients in the following major categories: reactive monomers and oligomers, crosslinkers, non-reactive diluents, photoinitiators and additives. Each material has its unique role in the resist formulation.

Reactive Monomers and Oligomers: Reactive monomers and oligomers are low molecular weight short-chain polymers. In the representative example, the di-epoxy oligomer cross-links with the epoxy group on another di-epoxy oligomer. Usually oligomers determine the film properties after curing. The silicone epoxy oligmer that we use will give us films with low surface energy after curing, thus helps mold-release after imprinting and curing. Typical fraction of oligomers in the UV curable liquid formulation is 94% (not counting the diluents).

Non-reactive diluents: If necessary, non-reactive diluents will be added to lower the viscosity of the uncured material to achieve thin resist films. Non-reactive diluents include typical high-boiling point (>80°C) solvents such as PGMEA. The more the diluents in the formulation, the thinner the film will be. The actual fraction of the diluents will depend on the application.

Cross-linker: A Cross-linker is a molecule with multiple reactive functional groups. It reacts with the reactive monomers or oligomers to form a cross-linked network. We use silicone epoxy with four cycloaliphatic epoxy groups as the cross-linker. The concentration in the formulation is typically 5%.

Cationic Photoinitiators: Cationic photoinitiators are chemicals that undergo actinic decomposition upon exposure of UV radiation to produce active cationic species (cations), such as super strong protons (H^+), that are capable of inducing cross-linking between the unsaturation sites of monomers and oligomers. The cationic photoinitiators include diaryliodonuim and triarylsulfonium salts, and are typically present at about a few percent by weight in the UV curable liquid formulation (not counting the non-reactive diluents).

Additives: Those ingredients are chemicals specifically added into the resist to modify its physical and chemical properties. They usually do not integrate into the crosslinked polymer network and only used with very small amount. The most common additives are stabilizers, adhesion promoters, and mold release agents. Stabilizers are used to prevent gelation in storage and premature curing due to low levels of light exposure; the adhesion promoters, such as 3-glycidoxypropyltrimethoxysilane, are utilized to improve the surface adhesion of the substrate; whereas the release agents to reduce the surface energy of the contact surfaces.

Film Preparation

Before nanoimprinting, a thin film of UV curable liquid is spin-coated on substrates such as silicon or glass. Due to high interfacial surface energy between epoxy functional silicone resist and substrates, typically film dewetting will occur during spin-coating, especially for the thin films. To overcome this problem, we coat the substrate with a layer of polymer film. Typically we use high-molecular weight PMMA and PS as the under-coating layer. They prove to be very effective in preventing the dewetting, thus enable us to achieve UV curable liquid film with good uniformity and a thickness ranging from microns to sub-100 nm. Because PMMA and PS can be easily removed by common organic solvents such as acetone, using them as under-coating layer will enable lift-off process, which is typically difficult in the currently available UV curable liquid resists. By varying the ratio of UV curable liquid material to diluents, we can achieve thin films with a thickness ranging from sub-100 nm to several microns. This could satisfy almost any kind of application requirements.

Experimental Results

Since the resist is a low viscous liquid spin-coated the substrate before curing, nanoimprinting such material only requires low pressure at relatively low temperature (below 80 °C). The pressure required is very low (less than1 atmospheretic pressure). This enables nano-patterning using conventional photolithography contact aligners. The mold is made from UV transparent material such as fused silica. After imprinting and UV flood exposure, the mold and the substrate are separated and a replica of the mold pattern will be imprinted into the resist. After removing the residual layers in the recessed pattern region, a lift-off process can be carried out.

Other properties

Film shrinkage: It is commonly observed that polymerization induced shrinkage can occur during the liquid to solid state phase transition. Among all the UV curable systems based on different chemistries, epoxy based cationic curing shows the lowest shrinkage. The film shrinkage of our formulation is assessed by measuring the film thickness change before and after curing. The film thickness is measured by ellipsometer. No more than 3% of shrinkage is observed, which is consistent with the general consensus on epoxy material. Our measurement shows that the average film shrinkage is 2%.

Oxygen reactive ion etching (RIE) property: Due to the silicon component of in the film, the cured resist shows very interesting oxygen RIE etching properties. For example, with the current material, a 20 nm layer is removed for the first 3 minutes of etching; but no more etching of the film is observed afterwards. This is possible due to the formation of silicon oxide on the top layer of the film after the oxygen plasma etching treatment, which acts as a hard mask to shield the inner part of the film from being attacked by oxygen plasma. This property is very useful because it will impart the film with much higher etching selectively than common organic based nanoimprint resist such as PMMA and PS. It also removes the constraint of the thickness of the undercoating layer.

Fluorine-containing RIE property: Fluorine-containing gases such as CHF_3 can be used to remove the residual layer after imprinting. The etching rate is measured to be ~ 14 nm/min. The etching condition used for the measurement is CHF_3 20 sccm, 20 mTorr pressure and 150 W power.

CLAIMS

What is claimed is:

1. A material for nanoscale contact printing, and for nano- and microlithography using simple contact exposure tools or other appropriate equipments at a low pressure and a low temperature comprising of the following components:

    a. A monomer containing cationically polymerizable functional groups;

    b. A crosslinker that contains multiple cationically polymerizable functional groups;

    c. A cationic photoinitiator

2. The material as set forth in claim 1, wherein in component (a) said monomer is any molecule containing high etch resistant components, wherein the high etch resistant component is:

    a. an organic component containing high C/H ratio organic groups, such as phenyl, norbornane, etc., or

    b. an organosilicone or organosilicone monomer containing (SiR_2O) or ($SiO_{3/2}$) unit, where R is H, methyl, phenyl, or any other hydrocarbon and fluorocarbon groups; preferably, methyl group.

3. The material as set forth in claim 1, wherein in component (a) said cationically polymerizable functional groups is any cationically polymerizable functional group, preferably, epoxy and vinyl ether groups.

4. The material as set forth in claim 1, wherein in component (b) said crosslinker is either an organic or silicone based molecule containing three or more cationically polymerizable functional groups, preferably, epoxy and vinyl ether groups.

5. The material as set forth in claim 1, wherein in component (c) said cationic photoinitiator is a chemical that undergoes actinic decomposition upon the exposure of UV radiation to produce active cationic species, such as, diaryliodonuim and triarylsulfonium salts bearing anions such as BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, $(C_6F_5)_4B^-$.

6. An appropriate under-coating layer, preferably from a polymer material that can be dissolved by typical organic solvent, is used to ensure film uniformity of the material as set forth in 1, and to enable a lift-off fabrication process.

7. The material as set forth in claim 1 is applied on the substrate to form a uniform thin film by spin-coating, dip-coating, spray-coating or other appropriate coating methods.

8. The material as set forth in claim 1 may be mixed with non-reactive diluent(s) to lower its viscorsity, wherein the diluents are typically high boiling point organic solvents, such as PGMEA, PGME, 2-heptanone, xylene, etc.

9. The material as set forth in claim 1 may be mixed with additives, such as adhesion promoters or mold release agents.

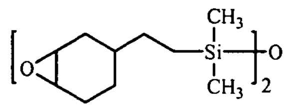
10. The low pressure as set forth in claim 1 is any pressure that is less than 10 atmospheric pressure.

11. The low temperature as set forth in claim 1 is a temperature between 0 to 100 oC, preferably, 20-60 o C.

12. The material system as set-forth in claim 1 is a suitable resist for the combined-nanoimprint-and-photolithography technique.

ABSTRACT OF THE DISCLOSURE

This invention presents a spin-on UV-curable silicone material for nanoscale contact-printing, and for nano- and microlithography using simple contact exposure tools or other appropriate equipments. This material comprises of these components: epoxy functional monomers and oligomers, epoxy functional cross-linkers, cationic photoiniators, and optionally non-reactive diluents and other additives. By using an appropriate material as a thin undercoating layer, this liquid resist can be spin-coated onto a variety of substrates with high uniformity with precisely controlled thickness across the whole substrate. The low viscosity of this liquid system allows imprinting with a low pressure at a lower temperature (less than 100 °C). Adding organosilicone components to the resist formulation will not only impart the resist with higher dry etching resistance but also provide lower surface energy, making it easier to be separated from the mask. These properties enable large-area high-throughput patterning of micro- and nanostructures or a combination of both. It also allows step-and-repeat patterning across very large wafers. This material system is also suitable for the Combined-Nanoimprint-and-Photolithography technique that we have developed (pending PCT application), which can greatly simplify the process of patterning nanostructures.



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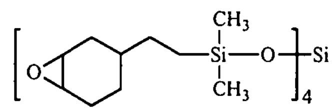

(II)

Fig. 1.

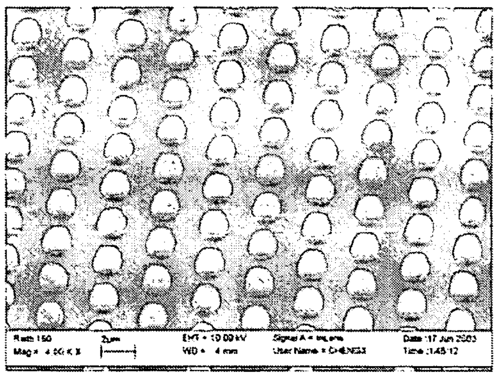

Fig. 2. One micron dot patterns

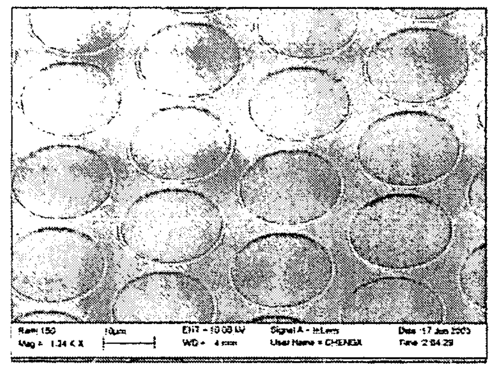

Fig. 3. 20 micron circular patterns

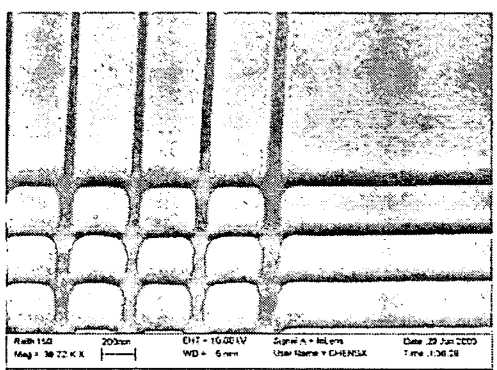

Fig. 4. 50 nm wide gaps

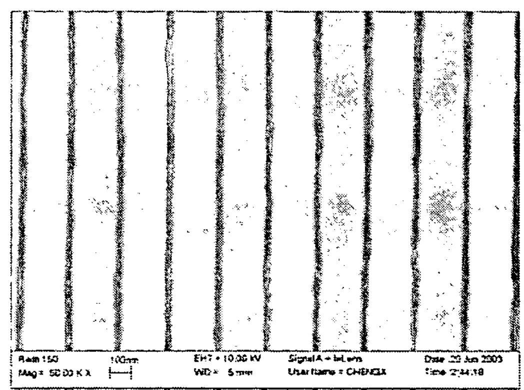

Fig. 5. 20 nm wide gaps

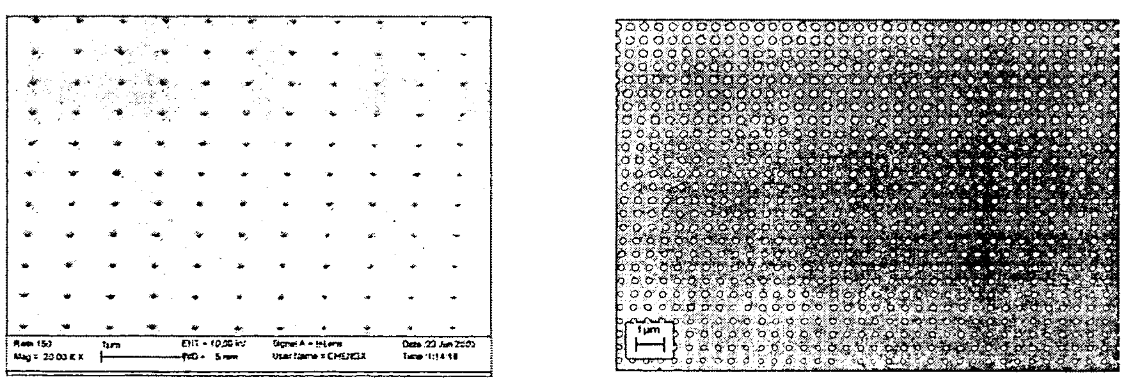

Fig. 6. (a) patterned 50 to 100nm diameter hole arrays, and (b) the corresponding Au nanodot arrays produced by a lift-off process

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